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# "Interfacial Instabilities: Part B - Oscillatory Phenomena and Waves"

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# INTERFACIAL INSTABILITIES

## PART B- OSCILLATORY PHENOMENA AND WAVES

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**Abstract**—Dispersion relations are derived for transverse and longitudinal waves appearing at the open surface of a liquid. Also provided here, in each case, are the values of the elasticity solute Marangoni number sufficient to sustain these oscillatory motions.

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## 1. INTRODUCTION

"Waves on a Liquid Surface" is the title of Chapter XI in the Physicochemical Hydrodynamics book by the late Ben Levich. Sections 120–122 specifically deal with the damping effect of surface active substances. In Section 120 he starts recalling that the ancient Greeks, as recorded by Pliny the Elder, knew "the effect of a surface active substance on wave motion", in "calming the fury of waves by means of oil poured on the surface of the sea". Levich goes on with arguments to support his hydrodynamic theory of the damping effect of sulutes. In this paper, in a modest way, we closely follow Ben's line of thought and asymptotic analysis in order to substantiate a hydrodynamic theory that helps sustaining waves by means of solutes. Thus, we explore a parallel path to that followed by Levich and from this perspective our study may represent one or two sections that Ben could have written had he had the time for revising and updating his PCH book.

We consider two types of wave motions. On the one hand *transverse*, capillary-gravity waves, directly related to the deformability of the open surface of a liquid. They originate when the equilibrium surface is disturbed, gets deformed and then forces tending to return it to the original state appear in the liquid. Capillary forces (Laplace over pressure) tend to reduce the increased surface. Besides, when liquid is in a gravitational field the disturbance also gives rise to gravitational forces that tend to return the surface to its original equipotential level state. Because of inertia, however, the liquid particles overshoot their original equilibrium position and, as a consequence, transverse waves develop along the liquid surface.

The other wave motions that we consider are *longitudinal* oscillations of the concentration of a surface-active solute along the liquid surface. Their existence is not surprising considering that a strong analogy is expected between a monolayer-covered surface and a stretched elastic membrane. The coverage with a solute either by adsorption from solution or by spreading, gives elastic properties to a liquid surface so that it can sustain the periodic surface expansion and compression, which accompanies longitudinal wave motion. These motions as well as the transverse waves may be induced by the Marangoni effect, i.e. by the variation of the surface tension with the solute concentration along the surface (Sternling & Scriven, 1959; Scriven & Sternling, 1960).

Generally, these waves or oscillatory motions are eventually damped, albeit differently, by the viscosity of the liquid (Cini *et al.*, 1987; De Voeght & Joos, 1984; Hansen & Ahmad, 1971; Linde *et al.*, 1979; Lucassen, 1968; Lucassen-Reynders & Lucassen, 1969; Van den Tempel & Van de Riet, 1965). For instance, for a frequency of oscillation $\Omega$ of a transverse wave and kinematic viscosity $\nu$, the viscous penetration length of the disturbance is of order $(\nu/\Omega)^{1/2}$. Thus, for deep enough liquid layers this viscous penetration is rather small with respect to the liquid depth. This is the case we consider here, thus limiting our analysis to a high enough frequency range such that $\Omega \gg \nu/h^2$, where $h$ is the depth of the liquid layer. For both types of wave we allow $h$ to reach infinity.

Transverse capillary waves or ripples cannot be explained unless we introduce the surface tension and thus, they have been called after Laplace. Longitudinal waves, on the other hand, can only be explained by introducing surface tension variation along the liquid surface. The inhomogeneity may be due to gradients of solute concentration or of temperature. Here we restrict consideration to solutes acting under isothermal conditions. We show that transverse and longitudinal waves can be sustained, rather than damped if using the Marangoni effect we maintain large enough gradients of solute in the liquid. Thus, the problem we address is that of stability of a quiescent liquid layer open to the air, subjected to Marangoni stress at the surface. We provide threshold values, in terms of the solute Marangoni number, and dispersion relations for transverse and longitudinal waves. Needless to say, the latter incorporate the results given in Ben Levich's book, while the former, is the genuine extension provided here.

The paper is organized as follows. Section 2 deals with the disturbance evolution equations, boundary conditions and definition of the relevant dimensionless groups entering the problem. In Section 3 we show the straightforward, albeit drastically simplified solution of the problem in two extreme approximations. We provide, however, the correct dispersion relations for both transverse and longitudinal waves. Section 4 accounts for numerical results obtained with the computer. In Section 5 we provide the analytical approach to the general case and compare with the numerical results from Section 4. Section 6 is devoted to some concluding remarks.

## 2. DISTURBANCE EQUATIONS

The linearized equations that disturbances upon the quiescent state obey are (Levich, 1962; Miller & Neogi, 1985):

$$\operatorname{div} v = 0 \tag{2.1}$$

$$\rho(\partial v/\partial t) = -\operatorname{grad} p + \mu\nabla^2 v \tag{2.2}$$

$$(\partial K/\partial t) - \beta_0(\partial w/\partial z) = D\nabla^2 K. \tag{2.3}$$

These disturbances also obey the following linearized boundary conditions (b.c.) at the open surface equilibrium position located at $z = 0$:

$$(\partial \xi/\partial t) = w \quad \text{(kinematic condition)} \tag{2.4}$$

$$(\partial\sigma/\partial\Gamma)\nabla_\Sigma\gamma + \mu(\nabla_\Sigma w + \partial u/\partial z) = 0 \tag{2.5}$$

$$p - \rho g\xi + \sigma_0\nabla_\Sigma^2\xi + 2\mu(\partial w/\partial z) = 0 \tag{2.6}$$

$$(\partial\gamma/\partial t) + \Gamma_0 \operatorname{div}_\Sigma u_\Sigma - D_\Sigma\nabla_\Sigma^2\gamma + D(\partial K/\partial z) = 0 \tag{2.7}$$

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$$\gamma = k^1(K-\beta_0\zeta)|_\Sigma, \tag{2.8}$$

where $v$ denotes velocity (components $u$, $v$, $w$); $\rho$, density; $p$, pressure; $K$, concentration of the solute; $\mu$, the dynamic viscosity ($\mu = \rho v$, with $v$ kinematic viscosity); $D$, mass diffusivity of the solute; $\zeta$ deformation of the open surface; $\sigma$, air–liquid interfacial tension ($\sigma_0$ denotes a suitable reference value); $g$, gravitational acceleration; $\Gamma$, excess solute concentration ($\Gamma_0$ is a suitable reference value); $\gamma$, disturbance upon $\Gamma$; $k^1 = (\partial\Gamma/\partial K)_0$ is Langmuir's adsorption constant (Davies & Rideal, 1963); $\beta_0 = (\partial K/\partial z)_0$, the solute gradient in the liquid; and the subscript $\Sigma$ accounts for differentials along the open surface. $(x, y)$ account for horizontal coordinates and $z$ is the vertical one.

With equation (2.4) we assume that a fluid particle follows the air–liquid interface in a way that there is no cavitation. Equation (2.5) accounts for the Marangoni stresses at the surface and it corresponds to the tangential stress balance. Equation (2.6) is the normal stress balance where we see the role played by the deformation of the surface both in the hydrostatic pressure and the Laplace over-pressure. Equation (2.7) accounts for the solute adsorption and diffusion to and along the surface. Equation (2.8) describes Langmuir's adsorption law in the linear approximation.

Now for universality in the presentation we change units and rescale all quantities, thus rendering them dimensionless. The capillary length:

$$l = (\sigma_0/\rho g)^{1/2} \tag{2.9}$$

is chosen as the unit of length. Then $v/l$, $l^2/v$, $\rho v^2/l^2$, $\beta_0 l$ and $\Gamma_0$ are, respectively, the new units for velocity, time, pressure, solute concentration and excess solute concentration at the surface. Using *bars* over the quantities in the dimensionless form equations (2.1)–(2.8) become:

$$\operatorname{div} \bar{v} = 0 \tag{2.10}$$

$$(\partial\bar{v}/\partial\bar{t}) = -\operatorname{grad} \bar{p} + \nabla^2\bar{v} \tag{2.11}$$

$$(\partial\bar{K}/\partial\bar{t}) - \bar{w} = S^{-1}\nabla^2\bar{K} \tag{2.12}$$

$$(\partial\bar{\xi}/\partial\bar{t}) = \bar{w} \tag{2.13}$$

$$(HE/H_tS)\nabla_\Sigma^2\bar{\gamma} + (\nabla_\Sigma^2 - \partial^2/\partial\bar{z}^2)\bar{w} = 0 \tag{2.14}$$

$$\bar{p} - (Bo/SC)\bar{\xi} + (l/SC)\nabla_\Sigma^2\bar{\xi} + 2(\partial\bar{w}/\partial\bar{z}) = 0 \tag{2.15}$$

$$HS[(\partial\bar{\gamma}/\partial\bar{t}) + \operatorname{div}_\Sigma \bar{u}_\Sigma - S_\Sigma^{-1}\nabla_\Sigma^2\bar{\gamma}] + (\partial\bar{K}/\partial\bar{z}) = 0 \tag{2.16}$$

$$\bar{\gamma} = -(H_t/H)(\bar{K} - \bar{\xi})|_\Sigma, \tag{2.17}$$

where we have used the following dimensionless groups:

$$S = v/D \quad \text{Schmidt number} \tag{2.18}$$

$$S_\Sigma = v/D_\Sigma \quad \text{surface Schmidt number} \tag{2.19}$$

$$C = \mu D/l\sigma_0 \quad \text{capillary number} \tag{2.20}$$

$$Bo = \rho g l^2/\sigma_0 \quad \text{Bond number.} \tag{2.21}$$

Note that $Bo$ equal to unity defines the capillary length.

$$E = -(\partial\sigma/\partial\Gamma)_0(k^1\beta_0 l^2/\mu D) \quad \text{elasticity solute Marangoni number} \tag{2.22}$$

$$H = \Gamma/\beta_0 l^2 \quad \text{surface excess solute number} \tag{2.23}$$

$$H_t = k^1/l \quad \text{Langmuir adsorption number.} \tag{2.24}$$

As no confusion is now expected, in the following we disregard the bar over the quantities keeping in mind that all of them are dimensionless. Then, for the linear evolution problem (2.10)–(2.17) a general solution for waves of small amplitude has the form (see Levich, 1962, equations 121, 1–3):

$$w = (Ae^{az} + Be^{mz}) \exp(iax + \lambda t) \tag{2.25}$$

$$u = (iAe^{az} + imBe^{mz}) \exp(iax + \lambda t) \tag{2.26}$$

$$p = -(\lambda Ae^{az}/a) \exp(iax + \lambda t) \tag{2.27}$$

$$K = \{Ae^{az}/\lambda + [SB/\lambda(S-1)]\, e^{mz} + Fe^{qz}\} \exp(iax + \lambda t) \tag{2.28}$$

with $m = (a^2+\lambda)^{1/2}$ and $q = (a^2 + S\lambda)^{1/2}$. $a = a_x^2 + a_y^2$ is the Fourier wave number and
$x = (x, y)$. $\lambda$ is the time constant whose real part determines stability and whose imaginary
part ($Im\ \lambda = \omega$) accounts for overstability, i.e. for oscillatory disturbances. $A$, $B$ and $F$ are
arbitrary constants left undetermined at the linear approximation. In fact $F$ can be obtained
from $A$ and $B$. Our notation is slightly different from that used by Ben Levich.

The solutions must satisfy the b.c. Then from the normal stress balance (2.15) we get:

$$A[Bo + a^2 + \lambda SC(2a + \lambda/a)] + B[Bo + a^2 + 2mSC\lambda] = 0. \tag{2.29}$$

From the tangential stress balance (2.14)

$$2a^2A + B[m^2 + a^2 + Ea^2/\lambda S(S-1)] + FEa^2/S = 0. \tag{2.30}$$

From the excess solute balance condition (2.16)

$$A(a/\lambda - HSa) + B[H_tS(\lambda + a^2/S_\Sigma)/\lambda(S-1) - HSm + mS/\lambda(S-1)] \\ + F[H_tS(\lambda + a^2/S_\Sigma) + q] = 0 \tag{2.31}$$

## 3. TWO EXTREME CASES

At this point we note that setting $B = 0$ in the Fourier modes amounts to restricting
consideration to the potential (ideal) part of the expected flow field. The opposite case
is $A = 0$, which corresponds to the purely viscous and rotational approximation to the
solution.

If we set $B = 0$ and further use the high frequency approximation, $\omega \gg a^2$, we get

$$(Bo + a^2)a - \omega^2 SC = 0. \tag{3.1}$$

Equation (3.1) describes the dispersion relation for transverse (Laplace) capillary gravity waves. Going back to dimensional quantities and using then $\Omega = \omega v/l^2$ and $k = a/l$, we get

$$\rho\Omega^2 = \rho g k + \sigma_0 k^3 \tag{3.2}$$

with $\Omega$ in $s^{-1}$ and $k$ in $cm^{-1}$. Equation (3.2) is indeed the standard expression for the oscillation frequency in capillary gravity waves (Levich, 1962).

In the opposite extreme case $A = 0$ and assuming that $H \ll 1$, $H_t \ll 1$ and for the large wavelengths $\omega \gg a^2$, we find:

$$Ea^2 + \omega^2 S^{3/2} = 0. \tag{3.3}$$

Let us now use the surface elasticity modulus, $\varepsilon$, introduced by Lucassen and other authors (Lucassen, 1968; Hansen & Ahmad, 1971; Sanfeld *et al.*, 1979)

$$\varepsilon = \partial\sigma/\partial \ln \Sigma \approx -(E\mu D/\beta l^2)\Sigma(\partial K/\partial\Sigma), \tag{3.4}$$

where the surface area $\Sigma$ is such that:

$$\Sigma(\partial K/\partial\Sigma) \approx \beta^*/(k^2+i\omega/\nu)^{1/2}. \tag{3.5}$$

Note that $\varepsilon$ is indeed a measure of the resistance to stretching of the surface. In the absence of adsorption and appreciable volume-to-surface transport $\varepsilon \propto -\partial\sigma/\partial \ln \Gamma$. Using (3.5):

$$\varepsilon = -E\mu D/l^2(k^2+i\omega/\nu)^{1/2}. \tag{3.6}$$

Thus equation (3.3) becomes:

$$i\varepsilon k^2 = \mu(\nu/D)^{1/2}\Omega D(i\Omega/\nu)^{1/2}, \tag{3.7}$$

which incorporates, as a particular case, Lucassen's dispersion relation for *longitudinal* waves at the liquid surface (Lucassen, 1968).

In the next section we numerically solve the problem and derive the results in better quantitative terms. Moreover in Section 5 we again treat the general problem in analytical terms, thus completing the picture.

## 4. SUSTAINED WAVES AT THE OPEN SURFACE OF THE LIQUID: COMPUTER RESULTS

Let us now see whether or not we have the possibility of overstability in our problem. This would mean that equations (2.29) and (2.30) have a non-trivial solution when $Re\ \lambda = 0$ and $Im\ \lambda \equiv \omega \neq 0$. As the system of equations is homogeneous, we just need to set the determinant of the coefficients of $A$, $B$ and $F$ equal to zero. This gives:

$$Ea^2/S = I_2/I_1 \tag{4.1}$$

with

$$I_1 \equiv [H_t S(\lambda + a^2/S_\Sigma)+q][(Bo+a^2)\lambda + (\lambda SC/a)(2a^2+\lambda)^2 - 4a^2\lambda SCm] \tag{4.2}$$

and

$$I_2 \equiv (Bo+a^2)[(mS-q)/\lambda(S-1) - a/\lambda + HS(a-m)]$$
$$+(\lambda SC/a)(m^2+a^2)[(mS-q)/\lambda(S-1) - HSm] - 2mSCa(1-HS\lambda). \tag{4.3}$$

Now, in equation (4.1) we set $Re\ \lambda = 0$ and $Im\ \lambda = \omega$, and search for solutions. For negative values of $E$, Fig. 1 shows typical $(E, \omega)$ overstability curves. The minima of the two curves correspond to different frequencies and thus, generally different wavelengths. One of the minima corresponds to the capillary length whereas the other corresponds to much larger values. Note that between these two curves there is a crossover at a value $\omega_i$. As we change the capillary number $C$ (Fig. 2) the first curve does indeed change shape and, in particular, in the limit of a flat surface when $C$ vanishes the (critical) elasticity number corresponding to the above mentioned minimum diverges to infinity with the power law $|E_C^T| \propto C^{-3/4}$. This implies that as expected, no transverse wave can be excited in an underformable liquid surface.

The minimum of the second curve, however, is rather unaffected by the capillary number, i.e. by the surface deformation. Its minimum corresponds to the onset of overstability in the form of longitudinal waves as discovered years ago by Lucassen (1968). This type of overstable motion is drastically affected by the Langmuir adsorption number $H_t$ as can be seen in Fig. 3. On the one hand large values of $H_t$ favor the appearance of longitudinal waves, i.e. increasing $H_t$ is a destabilizing factor. On the other hand, if $H_t$ vanishes the

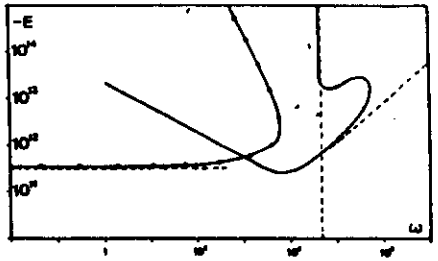

Fig. 1. Overstability $(-E, \omega)$ lines. Note that the vertical axis corresponds upside-down to negative values of the elasticity solute Marangoni number. $\omega$ is the dimensionless frequency. Solid lines correspond to transverse waves, and dotted lines to longitudinal oscillations (Section 4). Broken lines provide asymptotic results (Section 5). For illustration we have chosen $C = 10^{-11}$, $Bo = 1$, $H_t = 10^{-5}$, $H = -10^{-9}$, $S = 10^3$ and $S_\Sigma = 10^3$.

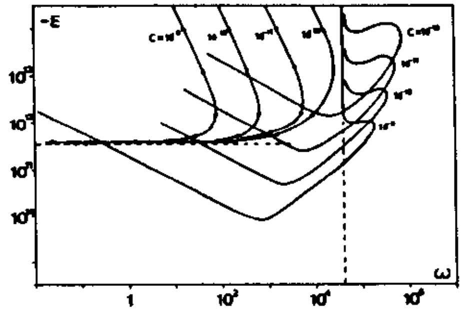

Fig. 2. Influence of capillary number, i.e. surface deformation upon overstability. $C$ really affects transverse oscillations. All other parameter values are as in Fig. 1.

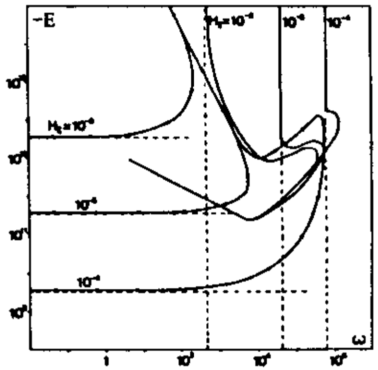

Fig. 3. Influence of Langmuir adsorption upon overstability. $H_t$ really affects longitudinal oscillations. All other parameter values as in Fig. 1.

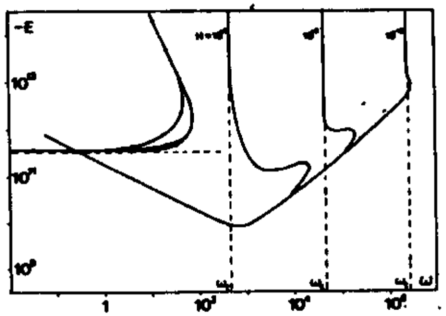

Fig. 4. Influence of surface excess solute number upon overstability. *H* really affects longitudinal oscillations. All other parameter values as in Fig. 1.

critical elasticity number $|E_C^L|$ diverges to infinity with the law $|E_C^L| \propto H_r^{-2}$. Note that for the transverse waves $E_C^T$ does not appreciably vary with $H_r$. Thus, we are faced with two different types of excitation as already indicated in Section 3 and extensively discussed by Lucassen (1968).

Note that as illustrated in Figs 1–3, above a certain frequency no oscillation is expected to be sustained. Thus cut-off frequency, $\omega_c$, decreases with increasing *H* (Fig. 4). High frequency excitations are easy to damp out when there is a film of accumulated solute at the liquid surface. The Schmidt number affects both transverse and longitudinal waves with, however, different power laws: $|E_C^T| \propto S^{1/4}$ and $|E_C^L| \propto S^{1/2}$. Transverse motions are essentially potential and thus, have an easier tendency to be sustained at low values of *S* (inertia dominates over dissipation). Longitudinal waves demand dissipation and are favored when *S* is large.

Finally, all the above results correspond to negative values of the elasticity solute Marangoni number. When this number is positive, i.e. when the mass transfer is from the liquid to the air it is known that, as in the case of heating a layer from the liquid side, the liquid tends to be destabilized through steady modes of convection (Bénard cells). However, some time ago Velarde *et al.* (1987) discovered that in the adsorptionless case there is an overstability branch for positive Marangoni numbers. Figure 5 shows how, for a deformable surface, this overstable mode appears when *E* is positive, in our case with solute adsorption. However, the wave is not of the standard Laplace type and moreover, for an infinitely extended layer, has no chance of appearance, as the cellular convection has a zero critical value at zero wave number. Thus, in the case of a finite layer, overstability may have a lower critical Marangoni number than cellular convection provided the capillary number, i.e. the surface deformation, is suitably chosen.

## 5. ANALYTICAL RESULTS CONCERNING TRANSVERSE AND LONGITUDINAL WAVES

Estimates of the various parameters entering the problem can be given for a standard liquid layer. Some of them depend on the actual value of the gravitational acceleration and thus, for illustration we consider two cases: the ground condition where *g* is about $10^3$ CGS units, and a reduced gravity spacecraft condition where the gravitational acceleration, compensated with the spacecraft centrifugal acceleration, reduces the actual acceleration to, say, one tenth of its normal ground value. Table 1 illustrates the parameter values chosen for $g = 10^3$ and $10^{-1}$ CGS units, respectively. Then for an asymptotic analysis we can take

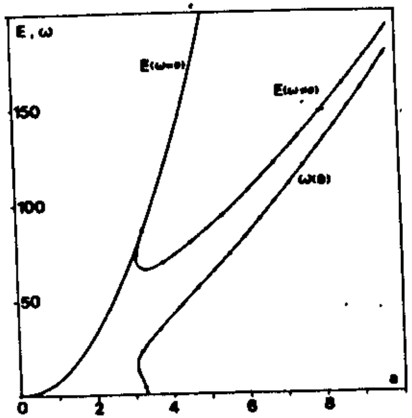

Fig. 5. Neutral stability lines (*E*, *a*) for *positive* Marangoni numbers. Solid and dotted lines correspond to steady instability and overstability, respectively. The latter is a transverse motion whose frequency is also given in the figure ($\omega$, $a$). Note that as we approach the neutrally steady branch the value of $\omega$ goes to zero, as expected. For illustration we have chosen $Bo = 1$, $C = 10^{-1}$, $S = 10^{-1}$, $S_\Sigma = 10^3$ and $H = H_r = 0$. When the latter two quantities are taken to be non-vanishing there is no qualitative change.

as a *smallness* parameter $\delta = S^{-1} = 10^{-3}$. With $O(\delta)$ denoting order of $\delta$ we can also use $S_\Sigma = O(\delta^{-1})$, $l = O(\delta^0)$, $C = O(\delta^3)$, $H = O(\delta^3)$ and $H_r = O(\delta^{5/3})$.

### 5.1. *Transverse waves*

In the high frequency approximation we can safely take $\omega = O(\delta^{-1})$ and $a = O(\delta^0)$. Then to the leading term in powers of $\delta$, equation (4.1) yields:

$$\begin{aligned} Ea^2/S = \{&(f_1^2 f_3/\omega^2 S^{1/2}) - [H_r f_1 f_2(\omega^2 S)^{1/2}/2^{1/2}] - 4a\omega SCf_2 f_3 \\ &+ if_1[f_2 f_3 + H_r f_1/(2\omega^3 S)^{1/2} + 4aCf_3 S^{1/2}/\omega]\}/(f_2^2 - f_1^2/\omega^2 S) \end{aligned} \tag{5.1}$$

with

$$f_1 = Bo + a^2 - \omega^2 SC/a \tag{5.2}$$

$$f_2 = a(Bo + a^2)/(\omega^3 S)^{1/2} \tag{5.3}$$

Table 1. Parameter values for a standard liquid layer for ground based and spacecraft based experiments. All quantities are in CGS units when applicable

| | Ground based experiments | Spacecraft based experiments |
|---|---|---|
| *g* | $10^3$ | $10^{-1}$ |
| *l* | $10^{-1}$ | 10 |
| *C* | $10^{-7}$ | $10^{-9}$ |
| *H* | $10^{-8}$ | $10^{-12}$ |
| $H_r$ | $10^{-4}$ | $10^{-6}$ |

and

$$f_3 = 1 + H_s(\omega S/2)^{1/2} \approx 1. \tag{5.4}$$

Neutral stability, and real values of the frequency $\omega$, require that the imaginary part of equation (5.1) vanishes. Then $f_1 = 0$, and equation (5.1) reduces to:

$$Ea^2/S = -4C\omega^3 S(2\omega S)^{1/2}[1+H_s(\omega S/2)^{1/2}]/(Bo+a^2) \approx -4a\omega(2\omega S)^{1/2}. \tag{5.5}$$

Equation (5.5) is the energy balance between viscous dissipation and surface tension work that, together with $f_1 = 0$, determines the neutral stability locus (Fig. 1).

The necessary condition for minimum in the neutral stability curve, $\mathrm{d}E/\mathrm{d}a = 0$, yields the threshold to sustain transverse waves at the open liquid surface in terms of the elasticity solute Marangoni number. We obtain:

$$E_C^T \approx -7.931(S/C)^{3/4} \tag{5.6a}$$

and

$$a_c = \sqrt{5}/5 \approx 0.4472 \tag{5.6b}$$

together with the oscillation frequency:

$$\omega_c \approx 0.7326/(SC)^{1/2}. \tag{5.6c}$$

These results agree with the numerical estimates obtained in Section 4 and are just the same as those obtained in the case of temperature gradients, provided we replace $S$ by the Prandtl number, $P$ (Garcia-Ybarra & Velarde, 1987). Moreover, as in the latter case the results reported here in the present paper have a direct relevance to experiments in microgravity conditions. Indeed, using (2.18) and (2.20)–(2.22), with $Bo = 1$ it follows that the actual solute gradient corresponding to (5.6a) scales with $g^{3/8}$ as $g$ goes to zero. This shows that the lower the *effective* gravity level is the lower is the gradient needed to excite and eventually sustain the oscillatory motion.

Finally, the actual solutions in the high frequency approximation are:

$$w_\Sigma = A \exp(ia_x x + ia_y y + \lambda t) \tag{5.7a}$$

$$u_\Sigma = A \exp(ia_x x + ia_y y + \lambda t + \pi/2) \tag{5.7b}$$

$$\zeta = (A/\omega) \exp(ia_x x + ia_y y + \lambda t - \pi/2) \tag{5.7c}$$

and

$$K_\Sigma = (A/\omega) \exp(ia_x x + ia_y y + \lambda t - 3\pi/4) \tag{5.7d}$$

thus showing that the solute concentration at the surface is phase shifted $\pi$ with respect to the surface horizontal velocity. The Marangoni effect is doing positive work. The $\pi/2$ phase shift between $w_\Sigma$ and $\zeta$ indicates how potential and kinematic energy are interchanged.

### 5.2. *Longitudinal waves*

The results obtained by earlier authors (Lucassen, 1968; Sanfeld *et al.*, 1979; Hennenberg *et al.*, 1979) help to guide us in the asymptotic approximation. Thus, choosing $\omega = O(\delta^{5/4})$ and $a = O(\delta^2)$ equation (4.1) becomes:

$$Ea^2/S = -\omega^2 S^{1/2} + i(\omega^3 S/2)^{1/2}[H_s\omega S^{1/2} - a(1+1/S^{1/2})]. \tag{5.8}$$

Again, as in the case of transverse motions we set the imaginary part of (5.8) to zero.

Then the elasticity solute Marangoni number or critical Marangoni number sufficient to sustain longitudinal waves is:

$$E_C^L \approx -\omega^2 S^{3/2}/a^2 \tag{5.9a}$$

with dispersion relation:

$$a_C \approx H_s \omega_C^L S^{1/2}. \tag{5.9b}$$

Combining (5.9a) and (5.9b) we get

$$E_C^L \approx -S^{1/2}/H_s^2, \tag{5.10}$$

which is the computer result reported in Section 4.

In this case within the long wave length approximation the solutions are:

$$(\partial w/\partial z)_\Sigma = Bm \exp(ia_x x + ia_y y + \lambda t) \tag{5.11a}$$

$$u_\Sigma = (Bm/a) \exp(ia_x x + ia_y y + \lambda t + \pi/2) \tag{5.11b}$$

and

$$K_\Sigma = (BmS/Ea^2) \exp(ia_x x + ia_y y + \lambda t - 3\pi/4) \tag{5.11c}$$

thus showing that due to the phase shift between $u_\Sigma$ and $K_\Sigma$, the surface tension work is positive and the oscillatory motion can be sustained.

## 6. CONCLUSION

Summing up the results found we can say that:

(i) Oscillatory motions either capillary gravity (Laplace) waves or longitudinal (Marangoni–Lucassen) waves can be excited and eventually sustained at the open surface of a liquid, provided there is transfer of a solute from the air to the liquid with solute accumulation at the open surface thus leading to Marangoni stresses there. The latter originate in the variation of surface tension with the concentration of the solute.

(ii) To sustain either type of wave we must go beyond a certain threshold in the elasticity solute Marangoni number. For transverse (Laplace) waves the threshold is approximately:

$$E_C^T = -7.931(S/C)^{3/4}, \tag{6.1}$$

whereas for longitudinal (Marangoni–Lucassen) waves it is:

$$E_C^L = -S^{1/2}/H_s^2. \tag{6.2}$$

Both thresholds are affected by the Schmidt number, $S$, which is the ratio of inertia to dissipation in the liquid (at vanishing $S$ inertia dominates, whereas at large enough values of $S$ inertia is rather irrelevant and dissipation dominates). For a given Schmidt number, the deformability of the open surface of the liquid is what matters for transverse waves, and this is accounted by the $C$-dependence in equation (6.1). However, as shown in equation (6.2), longitudinal waves are not affected by $C$. Rather, for a given Schmidt number it is the Langmuir's adsorption coefficient $H_s$ that matters in longitudinal waves.

(iii) Having shown that for solute transfer from air to the liquid both types of oscillatory motion may arise at the open surface of a liquid, the question now is which of them does really appear, i.e. what type of disturbance is sustained with the lower Marangoni threshold. The results obtained yield the following criterion. For:

$$S\left\{\begin{matrix} > \\ < \end{matrix}\right\} C^3/(7.931 H_i^2)^4 \text{ we have } \left\{\begin{matrix}\text{longitudinal} \\ \text{transverse}\end{matrix}\right\} \text{waves first.}$$

(iv) Finally, let us note for the record and without further discussion that, when the
transport of solute is from the liquid to the air there is yet another oscillatory type of
behavior of the open surface; its dispersion relation does not correspond to the standard
transverse wave, though it is related to the deformation of the open surface. Besides, it
appears in a parameter region where steady cellular motions are also expected very much
like in thermal Bénard convection, as already reported by Velarde *et al.* (1987).

In conclusion, we can say that our theory substantiates the claim made in the Intro-
duction: in parallel with sections dealing with the damping effect of solutes at the open
surface of a liquid we now have sections illustrating how this damping can be overcome
and how waves are eventually sustained, provided we take advantage of the Marangoni
effect, i.e. of the variation of the air–liquid surface tension with the concentration of a
solute along the open surface of the liquid. Sustained transverse or longitudinal waves are
in our case, nothing more than the result of instability, overstability of a liquid layer open
to the ambient air and subjected to solute transport from the air to the liquid, to the
existence of a gradient of solute concentration in the liquid and to the eventual adsorption
at the open surface thus leading to Marangoni stresses there.

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# THE HARMONIC OSCILLATOR APPROACH
# TO SUSTAINED GRAVITY-CAPILLARY (LAPLACE) WAVES AT LIQUID INTERFACES

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Sustained transverse (Laplace) gravity-capillary waves at a liquid–liquid interface are described as the harmonic oscillations of the interface at vanishing damping. Threshold values and other relevant predictions are given in terms of the surfactant elasticity Marangoni number and the transport coefficients of the liquids.

Let us consider the deformable interface separating two liquids of different densities, viscosities and mass diffusivities and assume the problem to be two-dimensional i.e., with horizontal and vertical coordinates $x$ and $z$, respectively. If the liquid below is labelled *one* the evolution of infinitesimal disturbances upon the motionless state on either side of the liquid–liquid interface is given by the following dimensionless equations [1–5]

$$\frac{\partial u_i}{\partial x} + \frac{\partial w_i}{\partial z} = 0 \quad (i=1,2)\,, \tag{1}$$

$$\frac{\partial C_1}{\partial t} - w_1 = \frac{1}{S}\nabla^2 C_1\,, \tag{2a}$$

$$\frac{\partial C_2}{\partial t} - w_2 = \frac{N_D}{S}\nabla^2 C_2\,, \tag{2b}$$

$$\frac{\partial w_1}{\partial t} = -\frac{\partial p_1}{\partial z} + \nabla^2 w_1\,, \tag{3a}$$

$$N_\rho \frac{\partial w_2}{\partial t} = -\frac{\partial p_2}{\partial z} + N_\eta \nabla^2 w_2\,, \tag{3b}$$

with $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial z^2$ and where $C_i$ $(i=1, 2)$ denotes solutal or surfactant concentration in each volume, $w_i$ $(i=1, 2)$ is the vertical velocity along $z$, $u_i$ $(i=1,2)$ is the horizontal velocity along $x$ and $p_i$ $(i=1, 2)$ is the pressure. $S=\nu_1/D_1$ (Schmidt numbver) with $\nu$ and $D$ the kinematic viscosity and the mass diffusivity respectively. $N_D = D_2/D_1$, $N_\rho = \rho_2/\rho_1$ and $N_\eta = \eta_2/\eta_1$ with $\eta = \rho\nu$ the dynamic viscosity. Note that we have introduced only one of the two Schmidt numbers.

If from either side we allow for surfactant adsorption without considering however the surfactant accumulation at the interface and call $N_s$ the ratio of the corresponding Langmuir adsorption slopes [1–3] the following boundary conditions (b.c.) must be satisfied at $z=0$:

$$w_1 = w_2\,, \tag{4}$$

$$\frac{\partial w_1}{\partial z} = \frac{\partial w_2}{\partial z}\,, \tag{5}$$

$$B\xi - \frac{\partial^2 \xi}{\partial x^2} + CS(p_2 - p_1) - 2CS(N_\eta - 1)\frac{\partial w}{\partial z} = 0\,, \tag{6}$$

$$\frac{E}{S}\frac{\partial^2 (C_1 - \xi)}{\partial x^2} - \left(\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial z^2}\right)(N_\eta w_2 - w_1) = 0\,, \tag{7}$$

$$\frac{\partial C_1}{\partial z} = \frac{\partial C_2}{\partial z}\,, \tag{8}$$

$$C_1 - \xi = N_s (C_2 - \xi)\,, \tag{9}$$

where we also consider that the interfacial tension changes with the surfactant concentration.

$$E = -\frac{\partial \sigma}{\partial C_1}\frac{\beta_1 l^2}{\eta_1 D_1}$$

is the elasticity Marangoni number and $l$ is a given space scale in the problem. *This could be the capillary length but needs not to be so.* $B=gl^2(\rho_1-\rho_2)/\sigma_0$ is the Bond number with $\sigma_0$ a reference value for the interfacial tension and $g$ the gravitational acceleration. $C=\eta_1\rho_1/\sigma_0 l$ is the capillary number. Just for reference note that the capillary length is given by $l^2=\sigma_0/g(\rho_1-\rho_2)$ which corresponds to Bond number equal to unity. $\beta_i$ $(i=1, 2)$ is the surfactant gradient in phase "$i$".

Solutions of the problem can be sought in the form [1–7]

$$w_1=A_1e^{az}+B_1e^{m_1z}\,, \tag{10}$$

$$w_2=A_2e^{-az}+B_2e^{-m_2z}\,, \tag{11}$$

$$p_1=-\frac{\lambda A_1}{a}e^{az}\,, \tag{12}$$

$$p_2=-\frac{N_\rho\lambda A_2}{a}e^{-az}\,, \tag{13}$$

$$C_1=F_1e^{q_1z}+\frac{A_1}{\lambda}e^{az}+\frac{SB_1}{\lambda(S-1)}e^{m_1z}\,, \tag{14}$$

$$C_2=F_2e^{-q_2z}+\frac{A_2}{\lambda}e^{-az}+\frac{SN_D^{-1}B_2}{\lambda(SN_D^{-1}-N_\rho N_\eta^{-1})}e^{-m_2z}\,, \tag{15}$$

with

$$m_1^2=\lambda+a^2,\quad m_2^2=N_\rho N_\eta^{-1}\lambda+a^2\,,$$
$$q_1^2=S\lambda+a^2,\quad q_2^2=SN_D^{-1}\lambda+a^2\,.$$

Note that to simplify the notation we have omitted in eqs. (10)–(15) a common factor $\exp(iax+\lambda t)$, where $a$ is the horizontal Fourier wavenumber and $\lambda$ is the time constant whose real part determines stability. For purely oscillatory motions $\lambda=i\omega$ with $\omega$ the dimensionless frequency.

Obviously eqs. (3a) and (3b) must be valid at the deformable interface $z=\zeta(x, t)$. Adding these two equations and denoting by $w$ the liquid velocity at interface points, we obtain

$$(1+N_\rho)\frac{\partial w}{\partial t}=-\frac{\partial(p_1+p_2)}{\partial z}+\nabla^2w_1+N_\eta\nabla^2w_2\,. \tag{16}$$

Using now (6) and (7), eq. (16) becomes

$$(1+N_\rho)\frac{\partial^2\zeta}{\partial t^2}+\frac{B+a^2}{CS}a\zeta$$
$$=2a(N_\eta-1)\frac{\partial w}{\partial z}-2a^2w+2N_\eta\frac{\partial^2w_2}{\partial z^2}$$
$$-\frac{Ea^2}{S}(C_1-\zeta)\,, \tag{17}$$

where we have used at the interface $w=\partial\zeta/\partial t$ (kinematic condition).

For the evaluation of all terms in the r.h.s. of eq. (17) we must solve for $A_i$, $B_i$ and $F_i$ using the equations and b.c. given above. Then after using for simplicity the high frequency approximation $\omega\gg a^2$ and the fact that for most practical purposes the Schmidt number is much larger than unity, after some elementary albeit lengthy calculus, eq. (17) finally becomes

$$(1+N_\rho)\frac{\partial^2\zeta}{\partial t^2}+\frac{B+a^2}{CS}a\zeta$$
$$=\frac{a\sqrt{2\omega}}{N_\rho^{-1/2}N_\eta^{-1/2}-1}$$
$$\times\left(\frac{Ea^2(1-N_D^{1/2}N_\eta^{-1})}{\omega^2S^2(1+N_\eta^{-1}N_D^{-1/2})}-2\right)\frac{\partial\zeta}{\partial t}\,. \tag{18}$$

Note that interfacial disturbances in a real liquid penetrate about $(\nu/\omega)^{1/2}$ and thus for $(\nu/\omega)^{1/2}\ll 1$ the $\omega\gg a^2$ assumption is justified.

Eq. (18) is the harmonic oscillator equation for transverse motions, $\zeta(x, t)$, of the deformable liquid–liquid interface due to the Marangoni effect. Its damping coefficient vanishes with a suitable value of $E$. Then the dispersion relation is given by

$$(1+N_\rho)\omega^2=\frac{B+a^2}{CS}a\,. \tag{19}$$

Using now the expression for $N_\rho$, $B$, $C$, $S$, $a=lk$ and $\omega=\Omega l^2/\nu_1$, eq. (19) yields

$$(\rho_1+\rho_2)\Omega^2=(\rho_1-\rho_2)gk+\sigma_0k^3\,, \tag{20}$$

which is the standard dispersion relation relation for gravity-capillary waves at a liquid–liquid interface. For the air–liquid interface $\rho_2\approx0$, thus $\rho_1+\rho_2\approx\rho_1-\rho_2\approx\rho_1\approx\rho$. Note that $\Omega$ and $k$ have, respectively, the units of $s^{-1}$ and $cm^{-1}$.

For the damping coefficient in eq. (18) to vanish we must have

$$Ea^2(1-N_D^{1/2}/N_\eta)>0\,, \tag{21}$$

i.e.

$$\text{sign}(E)=\text{sign}(1-N_D^{1/2}/N_\eta)\,. \tag{22}$$

Generally the sign of the Marangoni number is given by the sign of the volume gradient of the surfactant $\beta_i$, say. Then if $\beta_1$ is positive, i.e., the mass flux is from liquid one to liquid two ($\beta_2$ has always the same sign as $\beta_1$) eq. (22) demands

$$\eta_2/\eta_1-\sqrt{D_2/D_1}>0\quad(\beta_1,\beta_2>0)\,. \tag{23}$$

If, however the gradient is negative we rather have

$$\eta_2/\eta_1-\sqrt{D_2/D_1}<0\quad(\beta_1,\beta_2<0)\,. \tag{24}$$

Then denoting by "f" and "t" the transport direction from *phase f* to *phase t* we see that (23) and (24) are just the same condition

$$D_f/D_t>(\eta_f/\eta_t)^2 \tag{25}$$

irrespective of the sign of the gradients. Condition (25) is the necessary condition to have sustained oscillations at the liquid–liquid interface. This is achieved when the Marangoni number reaches the *critical* value, i.e., the minimum value that produces a vanishing damping coefficient in eq. (18). This value is

$$E_c=-\frac{4SN_\eta(1+N_\eta^{-1}N_D^{-1/2})B^{1/2}}{C(1+N_\rho)(N_D^{1/2}-N_\eta)} \tag{26}$$

for a frequency

$$\omega_c=\frac{\sqrt{2}\,B^{3/4}}{\sqrt{SC(1+N_\rho)}} \tag{27}$$

and a wavenumber

$$a_c=\sqrt{B}\,. \tag{28}$$

Note that when $B=1$, i.e., when we take the capillary length as the length unit, eqs. (27) and (28) reduce to

$$\omega_c=\frac{\sqrt{2}}{\sqrt{SC(1+N_\rho)}}\quad\text{and}\quad a_c=1$$

respectively.

These are the dimensionless values of the parameters that correspond to the onset of *overstability* at the deformable liquid–liquid interface and constitute a generalization of particular results known in the literature [1,5–8].

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# DISSIPATIVE HYDRODYNAMIC OSCILLATORS. I. MARANGONI EFFECT AND SUSTAINED LONGITUDINAL WAVES AT THE INTERFACE OF TWO LIQUIDS.

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## ABSTRACT

The oscillatory motion of a liquid-liquid interface induced by the Marangoni effect, i.e., by the variation of surface tension with the concentration of a surfactant, is described as the harmonic oscillation of the surfactant concentration at the interface. Then, at vanishing damping, threshold values and parameter regions for sustained longitudinal (Marangoni-Lucassen) waves are given in terms of the transport coefficients of the two liquids.

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## 1. INTRODUCTION

Capillary waves -or ripples- and gravity waves have been well studied since Stokes [1-4]. Their properties -their dispersion relation and damping coefficient- were shown to be completely determined by the stress conditions at the liquid surface. Specially the major influence of the boundary condition for normal stress to the surface has been emphasized [1,2,5]. While ripples and gravity waves are rather transverse motions due to the deformability of the surface [1-4] there is yet another type of wave discovered years ago by Lucassen [5]. It refers to mostly longitudinal (or elastic) motions along the surface, in the limit along a flat surface. Their existence is not surprising considering that a strong analogy is expected between a monolayer-covered surface and a strecthed elastic membrane. The coverage with a surfactant monolayer-either by adsorption from solution or by spreading-gives indeed elastic properties to a surface so that it tends to resist the periodic surface expansion and compression which accompanies wave motion. The longitudinal wave, has received much less attention than the other type of motion since under most conditions occurring in practice they are damped out much more rapidly than are gravity-capillary waves. On the other hand the latter are also possible in ideal, viscous-free liquids (potential flow) while the longitudinal waves necessarily demand dissipation and viscosity [5].

Lucassen [5] showed that longitudinal waves are to a major extent related to the boundary condition for tangential stress with a frequency that depends on the liquid viscosity and the variation of surface tension with the concentration of the adsorbed surfactant, i.e. on the elasticity Marangoni number of the liquid surface. Gravity-capillary waves have a frequency that depends on gravity and on surface tension (Laplace overpressure) and not on viscosity. The latter coefficient only appears in the damping factor of the dispersion relation should the liquid considered be a viscous one. For these reasons gravity-capillary waves may be called after Laplace whereas the longitudinal ones should be called after Marangoni and Lucassen.

In the present note following the pioneering analysis given by Lucassen and other authors [5-10] we consider the role of the Marangoni effect, i.e., the variation of surface tension with the concentration of a surfactant on a liquid surface and we provide the dispersion relation of longitudinal (Marangoni-Lucassen) waves together with the dissipation threshold sufficient to sustain these oscillatory motions. Moreover we also provide here the parameter regions (in terms of viscosity and mass diffusivity) where they can be observed.

## 2. DISTURBANCE EQUATIONS.

Let us consider two liquid layers at rest with an interface between them located at $z = 0$; $z$ is the vertical coordinate say. Let $\eta$, $\nu$ ($\eta = \rho\nu$), D and $\rho$ denote the corresponding dynamic viscosity, kinematic viscosity, mass diffusivity and density in each liquid. we shall derote with subscript "one" the lower liquid. Let us assume that a surface active component (surfactant) is distributed in each bulk phase with a given volume gradient and that it may be adsorbed at the interface according to Langmuir's law [1]. Then if we consider disturbances at the interface that may eventually be amplified thus leading to interfacial instability the expected evolution of such disturbances is governed by equations valid on each side of the interface and at the interface itself. For the simplest two-dimensional problem in dimensionless form we have [1]

$$\operatorname{div} v_1 = \operatorname{div} v_2 = 0 \tag{2.1}$$

$$(\partial v_1/\partial t) + \operatorname{grad} p_1 - \nabla^2 v_1 = N_\rho (\partial v_2/\partial t) + \operatorname{grad} p_2 - N_\eta \nabla^2 v_2 = 0 \tag{2.2}$$

and

$$(\partial K_1/\partial t) - w_1 - S^{-1} \nabla^2 K_1 = (\partial K_2/\partial t) - w_2 - S^{-1} N_D \nabla^2 K_2 = 0 \tag{2.3}$$

where $v_i$ ($i = 1,2$) = ($u_i$, $w_i$) with u and w the horizontal and vertical velocity components of the disturbance velocity field. p denotes pressure. $S = \nu_1/D_1$ (Schmidt number). $N_D = D_2/D_1$, $N_\eta = \eta_2/\eta_1$. $N_\rho = \rho_2/\rho_1$. x accounts for the horizontal coordinate. K is the volume concentration of the surfactant.

Let $E = -(\partial\sigma/\partial K_1)\, \beta_1 l^2/\eta_1 D_1$ be the elasticity (solutal) Marangoni number with $\sigma$ the liquid-liquid interfacial tension. E is indeed a dimensionless measure of the variation of surface tension with the concentration of the surfactant. $\beta$ is the volume concentration gradient of the surfactant. l is a characteristic length in the problem that may very well be the capillary length but need not to be so. The capillary length is given by $l^2 = \sigma_0/(\rho_1 - \rho_2)g$ with $\sigma_0$ a reference value. $B = (\rho_1 - \rho_2)g\, l^2/\sigma_0$ is the Bond number. $C = D_1 \nu_1 \rho_1/\sigma_0 l$ is the capillary number. Then when surface deformation and surface accumulation of the surfactant can be neglected the

disturbance evolution equations (1) - (3) for longitudinal motions obey the following boundary conditions (b.c.) at $z = 0$ [1]

$$w_1 = w_2 = 0 \tag{2.4}$$

$$(\partial w_1/\partial z) = (\partial w_2/\partial z) \tag{2.5}$$

$$\left(\frac{E}{S}\right)\frac{\partial^2}{\partial x^2}K_1 + N_\eta\left(\frac{\partial^2 w_2}{\partial z^2}\right) - \frac{\partial^2 w_1}{\partial z^2} = 0 \tag{2.6}$$

$$\Gamma S\,(\partial K_1/\partial t) = \partial\,(K_2 - K_1)/\partial z \tag{2.7}$$

$$K_1 = N K_2 \tag{2.8}$$

where $\Gamma$ is the dimensionless Langmuir adsorption number [11], i.e., the slope of the Langmuir adsorption law at the interface per unit length l (in the two-dimensional problem). N is the ratio of $\Gamma_2$ to $\Gamma_1$ when $\Gamma$ is evaluated from either side of the interface.

Due to the linearity of the problem we may seek disturbances of the form

$$w_1 = B_1 (-e^{az} + \exp(m_1 z) \tag{2.9}$$

$$w_2 = B_2 (-e^{-az} + \exp(-m_2 z)) \tag{2.10}$$

$$P_1 = B_1 (\lambda/a)\, e^{az} \tag{2.11}$$

$$P_2 = -B_2 N_r (\lambda/a)\, e^{-az} \tag{2.12}$$

$$K_1 = R_1 \exp(q_1 z) - (B_1/\lambda)\, e^{az} + [B_1 S/\lambda(S-1)] \exp(m_1 z) \tag{2.13}$$

and

$$K_2 = R_2 \exp(-q_2 z) - (B_2/\lambda) e^{-az} + (B_2 S N_D/\lambda(S N_D^{-1} - N_\rho N_\eta^{-1})) \exp(-m_2 z) \tag{2.14}$$

where "a" denotes a Fourier mode and $\lambda$ a complex quantity whose imaginary part is a dimensionless frequency. $m_1^2 = \lambda + a^2$, $m_2^2 = N_\rho N_\eta^{-1} \lambda + a^2$, $q_1^2 = S\lambda + a^2$ and $q_1^2 = S\lambda N_D^{-1} + a^2$. The quantities $B_1$, $B_2$, $R_1$ and $R_2$ are the arbitrary disturbance amplitudes one of them is left undetermined in a linear theory.

Now let us take the time derivative of Eq. (7). We have

$$\Gamma S\,(\partial^2 K_1/\partial t^2) = \partial^2(K_1 - K_2)/\partial z\,\partial t \tag{2.15}$$

On the other hand taking the z-derivative in Eq. (3) we can estimate the right hand side of Eq. (15). However we must estimate terms like $\partial\nabla^2 K_i(i=1,2)/\partial z$. For such purpose we use the relationships given earlier. For instance, using (5) we get

$$B_2 = -(m_1 - a)\,B_1/(m_2 - a) \tag{2.16}$$

while using (6) and (7)

$$R_1 = -[B_1/\lambda(S-1)] - (\lambda S/Ea^2)[1 + N_\rho\,(m_1-a)/(m_2-a)]B_1 \tag{2.17}$$

and using (8)

$$R_2 = \frac{(m_1 - a)\,N_\rho\,N_\eta^{-1}}{(m_2 - a)\,\lambda\,(SN_D^{-1} - N_\rho\,N_\eta^{-1})}\,B_1 - \frac{\lambda S}{NE\,a^2}\left(1 + N_\rho\,\frac{m_1 - a}{m_2 - a}\right)B_1 \tag{2.18}$$

## 3. RESULTS.

We are not interested in the evolution of monotic disturbances but rather in oscillatory motions. For this reason we now set $\lambda = i\omega$, thus making $\lambda$ purely imaginary. Using (2.3), (2.16), (2.18), after some lengthy, albeit straightforward calculus, Eq. (2.15) becomes

$$(1+N_\rho^{1/2}N_\eta^{1/2})\,\Gamma S^{1/2}(d^2K_1/dt^2) + (2\omega)^{1/2}\left[(1+N_\rho^{1/2}N_\eta^{1/2})\left(1+\frac{1}{N_D^{1/2}N}\right) + \frac{Ea^2}{S^2\omega^2}\Pi_1\right]\frac{dK_1}{dt} +$$

$$+\,a\omega\left[(1+N_\eta)\left(1+\frac{1}{NN_D^{1/2}}\right) + \frac{E\alpha^2}{S^2\omega^2}\Pi_2\right]K_1 = 0 \tag{3.1}$$

with

$$\Pi_1 = \sqrt{\frac{N_\rho N_D}{N_\eta}} - 1 \tag{3.2}$$

and

$$\Pi_2 = N_D^{1/2} - 1 \tag{3.3}$$

Equation (3.1) is the simplest harmonic oscillator description of the longitudinal oscillations of the surfactant concentration along the interface. Thus increasing the value of the elasticity Marangoni number when the damping coefficient vanishes in Eq. (3.1) we have the possibility of sustained interfacial oscillations.

When the damping coefficient is set to zero we have the following two relationships

$$(1 + N_\rho^{1/2}N_\eta^{1/2})\left(1 + \frac{1}{N_D^{1/2}N}\right) + \frac{Ea^2}{S^2\omega^2}\Pi_1 = 0 \tag{3.4}$$

and

$$a\left[(1 + N_\eta)\left(1 + \frac{1}{N_D^{1/2}N}\right) + \frac{Ea^2}{S^2\omega^2}\Pi_2\right] = \omega\,(1 + N_\rho^{1/2}N_\eta^{1/2})\,\Gamma S \tag{3.5}$$

To be satisfied, Eq. (22) demands that

$$E\,\Pi_1 < 0 \tag{3.6a}$$

e.g.

$$\mathrm{sgn}\,(E) = -\,\mathrm{sgn}\left(\frac{N_\rho^{1/2}N_D^{1/2}}{N_\eta^{1/2} - 1}\right) \tag{3.6b}$$

that together with sgn (E) = sgn ( $\beta_1$) yields the following consequence: To have oscillatory behavior we must have

$$(D_f/D_t) > (\nu_f/\nu_t) \tag{3.7}$$

where "f" and "t" stand for "from" and "to", a way of indicating how the surfactant is being transported from and to the volume. Condition (3.7) is a condition for overstability in Marangoni convection obtained some time ago by Sanfeld and collaborators, [9]. However, contrary to their findings and due here to role of surfactant adsorption at the interface this condition is a necessary, albeit not sufficient condition for overstability. Further constraints must be satisfied and they are specified below.

Years ago Lucassen [5] introduced a complex elasticity modulus, $\varepsilon$, which is related to our elasticity Marangoni number by the following relationship

$$E = -\frac{\varepsilon l^2 (k^2 + i\,\Omega/\nu_1)^{1/2}}{\eta_1 D_1} = \frac{\varepsilon l^2 (i\,\Omega/\nu_1)^{1/2}}{\eta_1 D_1} \qquad (3.8)$$

with $a = kl$ and $\omega = \Omega\, l^2/\nu_1$. The quantity k can be assumed to be smaller than the inverse of the viscous penetration length. Then using these new variables, Eq. (3.4), reduces to

$$\varepsilon m k^2 + i\eta_1 \Omega m^2 (\nu_1/D_1) \frac{[1 + (\rho_2\eta_2/\rho_1\eta_1)^{1/2}][1 + N (D_1/D_2)^{1/2}]}{(\nu_1 D_2/\nu_2 D_1)^{1/2} - 1} = 0 \qquad (3.9)$$

with $m^2 = k^2 + i\Omega/\nu_1 \approx i\Omega/\nu_1$. Eq. (3.9) is a generalization of the particular case discussed by Lucassen [5] (see also Eq. (40.2) in Ref. [7])

Then using both Eqs. (3.4) and (3.5) we get

$$E_c = -\left[\frac{(N_D^{1/2} + N_\eta)(N_\rho^{1/2} N_\eta^{1/2} - 1)}{S\Gamma\Pi_1 \Pi_2}\right]^2 \left[\frac{(1 + N^{-1} N_D^{-1/2})\, S^2}{\Pi_1} (1 + N_\rho^{1/2} N_\eta^{1/2})\right] \qquad (3.10)$$

and the dispersion relation

$$\omega_c = a_c \frac{(N_D^{1/2} + N_\eta)(N_\rho^{1/2} N_\eta^{-1/2} - 1)}{S^{1/2}\Gamma \Pi_1 \Pi_2} \qquad (3.11)$$

The value $E_c$ is the minimal value of the elasticity Marangoni number needed to sustain longitudinal interfacial convective oscillations of frequency $\omega_c$. Using the fact that both $\omega$ and a must be positive numbers we get from (3.11) that the following relationship must be satisfied

$$(\nu_\ell/\nu_t) < 1 \qquad (3.12)$$

in order to have oscillations.

Thus putting together Eqs. (3.7) and (3.12) we have the sufficient conditions to sustain the longitudinal waves [5]. Our results generalize Lucassen's earlier finding as he only considered damped motions. Here we see that eventually with strong enough dissipation i.e. for Marangoni numbers larger than $E_c$ these longitudinal oscillations can be sustained along the interface even if it is not deformed. On the other hand our results delineate a more restricted domain of (surfactant-induced) interfacial oscillations than the domains reported by earlier authors [9,10]

## ACKNOWLEDGMENTS.

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# NONLINEAR TRANSVERSE OSCILLATORY MOTIONS AT THE OPEN SURFACE OF A LIQUID LAYER SUBJECTED TO THE MARANGONI EFFECT

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## ABSTRACT

The simplest nonlinear description of sustained capillary-gravity waves at the open surface of a liquid layer heated from above or below (according to the liquid used) is here provided. Results are given for specific values of the parameters involved in the problem (Marangoni, capillary and Prandtl numbers) as well as the discussion of an experiment that under microgravity conditions aboard a spacecraft can in clear-cut way test the validity of our predictions.

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Disturbances at an air-liquid interface can develop in various ways. Either as a steady convective pattern like in Bénard convection[1] or in the form of oscillatory motions (standing waves, travelling waves, etc.). The latter could be transverse capillary-gravity waves or longitudinal motions, *e.g.*, oscillatory variations of the concentration of a surfactant along the air-liquid interface that practically remains level. We shall restrict consideration here to the former case.

Recently, the onset of overstability and the possibility of sustaining transverse oscillations in a Bénard layer has been explored by one of the authors[2]. A similar problem for a liquid-liquid interface when the interface can acommodate a surfactant has been studied by the present authors[3]. Both studies correspond to a linear stability analysis of the problem and already in Ref. 2 it was pointed out the relevance of the findings to experiments under micro/low-gravity conditions. However, in order to assess the eventual saturation of the oscillatory instability predicted in Refs. 2 and 3 we must explore the nonlinear evolution of the oscillation. Thus in the present note we concentrate on the simplest nonlinear approach to the description of the transverse motions induced by the thermal Marangoni effect in a Bénard layer.

For the two-dimensional geometry considered in Ref. 2, *i.e.*, a Bénard layer heated from above if we start from a motionless steady state the nonlinear thermohydrodynamic evolution of the liquid layer is given by the following disturbance equations

$$\frac{\partial u}{\partial x}+\frac{\partial w}{\partial z}=0 \qquad (1)$$

$$\frac{\partial w}{\partial t}+u\frac{\partial w}{\partial x}+w\frac{\partial w}{\partial z}=-\frac{\partial p}{\partial z}+\nabla^2 w \qquad \cancel{(1)}\ (2.a)$$

$$\frac{\partial u}{\partial t}+u\frac{\partial u}{\partial x}+w\frac{\partial u}{\partial z}=-\frac{\partial p}{\partial x}+\nabla^2 u \qquad \cancel{(2)}\ (2.b)$$

and

$$\frac{\partial \theta}{\partial t}+u\frac{\partial \theta}{\partial x}+w\frac{\partial \theta}{\partial z}=w+P^{-1}\nabla^2\theta \qquad (3)$$

together with the following boundary conditions

$$\frac{\partial \xi}{\partial t}=w-u\frac{\partial \xi}{\partial x} \qquad (4)$$

$$p-\frac{Bo}{CP}\xi+\frac{1}{N^3}\left(\frac{1}{CP}-\frac{M}{P}(\theta-\xi)\right)\frac{\partial^2\xi}{\partial x^2}=\frac{2}{N^2}\left(\frac{\partial w}{\partial z}-\left(\frac{\partial u}{\partial z}+\frac{\partial w}{\partial x}\right)\frac{\partial \xi}{\partial x}+\frac{\partial u}{\partial x}\left(\frac{\partial \xi}{\partial x}\right)^2\right) \qquad (5)$$

$$-\frac{M}{P}\left(\frac{\partial(\theta-\xi)}{\partial x}+\frac{\partial\theta}{\partial z}\frac{\partial\xi}{\partial x}\right)=\frac{1}{N}\left\{\left(\frac{\partial u}{\partial z}+\frac{\partial w}{\partial x}\right)\left[1-\left(\frac{\partial\xi}{\partial x}\right)^2\right]+4\frac{\partial w}{\partial z}\frac{\partial\xi}{\partial x}\right\} \qquad (6)$$

and

$$\frac{\partial\theta}{\partial z}=0 \qquad (7)$$

where according to (7) we have prescribed the heat flux at the open surface. The following symbols and dimensionless groups have been introduced: (u,w), horizontal and vertical velocity disturbances; p, pressure disturbance; ξ, interfacial deformation with respect to the level position; T, temperature; θ: temperature disturbance; β, temperature gradient;

$$N=\sqrt{1+\left|\frac{\partial\xi}{\partial x}\right|^2}$$

$M=(-\partial\sigma/\partial T)\beta\ell^2/\kappa\nu$, thermal Marangoni number; $C=(\rho\nu\kappa/\sigma\ell)$, capillary number; $P=\nu/\kappa$, Prandtl number, $Bo=(\rho g\ell^2/\sigma)$, Bond number; ρ, density; σ, air-liquid interfacial tension; g, gravitational acceleration; ℓ, a suitably chosen length scale (this may be taken as the capillary length but need not to be so); ν, kinematic viscosity and κ, thermometric conductivity.

The air is assumed to be passive and weightless with respect to the liquid.

The simplest approach to the above posed nonlinear problem is the single-mode analysis which is expected to be a useful description in a small enough neighborhood of the onset of overstability. Moreover, the more we move into low gravity the larger the capillary length becames thus providing greater relevance to the single mode approximation. On the other hand, transverse interfacial disturbances are expected to penetrate little in the liquid; the penetration depth depends indeed on the wavelength and frequency excited and on the viscosity of the liquid. The latter assumption gives relevance to the 'potential' flow approximation to the time-dependent convection or in other terms to the limitation of the study to the high-frequency motions only. Thus for an arbitrary disturbance $f(x,z,t)$ we set $f(x,z,t) \sim f(z,t)\exp(iax)$ and $\omega_0^2=(Bo+a^2)a/CP$. The latter is Laplace law (potential flow). These two assumptions are based on the analysis given in Ref. 2. Using them Eq. (4) becomes

$$\frac{\partial\xi}{\partial t}=w+\xi\frac{\partial w}{\partial z} \qquad (8)$$

On the other hand Eq.(1) at $z=\xi$ is

$$\frac{\partial w}{\partial t}=-\frac{Bo+a^2/N^3}{PC}a\xi+\frac{M}{PN^3}(\theta-\xi)a^3\xi-2a\frac{(1+a^2\xi^2)}{N^2}\frac{\partial w}{\partial z}-a^2\left(1+\frac{2a\xi}{N^2}\right)w+\left(1-\frac{2a\xi}{N^2}\right)\frac{\partial^2 w}{\partial z^2} \qquad (9)$$

Note that neglecting the nonlinear terms and using the high frequency approximation, $\omega_0 \gg a^2$, Eq.(9) yields, as expected, the (Laplace) harmonic oscillator equation (for zero damping)

$$\frac{\partial^2\xi_0}{\partial t^2}+\frac{Bo+a^2}{CP}a\xi_0=0 \qquad (10)$$

The zeroth-order (linear) disturbances are, $\xi_0$,

$$w_0=\frac{\partial\xi_0}{\partial t}e^{az} \qquad (11)$$

and

$$\theta_0=\xi_0 e^{az}+\frac{a}{\sqrt{2P\omega_0}}\left(\frac{1}{\omega_0}\frac{\partial\xi_0}{\partial t}-\xi_0\right)e^{\sqrt{2P\omega_0}\,z} \qquad (12)$$

where $\omega_0$ denotes the harmonic frequency in (10) and the subscript 'zero' describes the linear solutions.

Consideration now of the nonlinear terms in Eqs. (8) and (9) up to cubic terms leads to

$$\frac{d\xi}{dt}=w(1+a\xi) \qquad (13)$$

and

$$\frac{dw}{dt} = -\frac{Bo+a^2}{CP}a\xi + \frac{Ma^3}{P\omega_0\sqrt{2P\omega_0}}\left(\frac{d\xi}{dt} - \omega_0\xi\right)\left[-1 + 3a\xi + \frac{5}{2}a^2\xi^2\right]$$

$$-4a^2\left[1 + 2a\xi(1 - 2a\xi)\right]w + \frac{3a^5}{2CP}\xi^3 \qquad (14)$$

which after reduction to a single differential equation become

$$\frac{d^2\xi}{dt^2} + \delta\frac{d\xi}{dt} + \left[\omega_0^2 - \omega_0(\delta - 4a^2)\right]\xi = -\omega_0^2 a\xi^2 + a\left(\frac{d\xi}{dt}\right)^2 + (\delta - 4a^2)\left(\frac{d\xi}{dt} - \omega_0\xi\right)2a\xi$$

$$-8a^3\xi\frac{d\xi}{dt} - a^2\xi\left(\frac{d\xi}{dt}\right)^2 + \frac{11}{2}a^2\xi^2(\delta - 4a^2)\left(\frac{d\xi}{dt} - \omega_0\xi\right) + 16a^4\xi^2\frac{d\xi}{dt} + \frac{3a^5}{2CP}\xi^3 \qquad (15)$$

where

$$\delta = \frac{Ma^3}{\sqrt{2}\,(P\omega_0)^{1/2}} + 4a^2 \qquad (16)$$

At $\delta = 0$ we have overstability from the linear analysis. Positive (respectively, negative) values of $\delta$ account for subcritical (respectively, supercritical) motions.

For universality in the presentation it is useful to rescale both space and time. Thus, with $\zeta = a\xi$ and $\tau = \omega_0 t$, and using the high-frequency limit (here $\omega_0 \gg a^2 (\sim 1)$ with $\omega_0^2 (\sim 1/CP$, Eq. (15) reduces to

para el crucial

para el L.C.

X Nonlinear oscillator

$$\boxed{\frac{d^2\zeta}{d\tau^2} + \Delta\frac{d\zeta}{d\tau} + \zeta = -\zeta^2 + \alpha\zeta^3 + \left(\frac{d\zeta}{d\tau}\right)^2 - \beta\zeta\frac{d\zeta}{d\tau} - \zeta\left(\frac{d\zeta}{d\tau}\right)^2 - \gamma\zeta^2\frac{d\zeta}{d\tau}} \qquad (17)$$

where $\Delta = \delta/\omega_0$, $\alpha = 3a^3/2CP\omega_0^2$, $\beta = 16a^2/\omega_0$ and $\gamma = 6a^2/\omega_0$. Thus Eq.(17) is the simplest equation describing the limit cycle oscillations of the air-liquid interface. We have checked that indeed Eq.(15) as well as Eq.(17) possess a *limit cycle* solution. This has been done both with the computer and using the time-derivative (singular perturbation) expansion procedure[4].

The time-derivative expansion procedure[4] permits to obtain in a perturbative scheme both the amplitude and the period of the oscillation in terms of the initial condition and thus to assess the stability of the limit cycle. *On the one hand* it can be shown that the limit cycle bifurcates supercritically for $\Delta$ (or $\delta$) negative, *i.e.*, we have a supercritical Hopf bifurcation, and *on the other hand* one obtains the amplitude,

$$\zeta^2_{max} = -\frac{2\delta}{3a^2} \qquad (18)$$

Figures 1 and 2 depict the results found. Fig.1, obtained using Eq.(15), shows the approach to the limit cycle from inside and outside. These are numerical results using the computer. In Fig.2 we compare the (exact) computer (numerical) result using Eq.(17) and the second-order perturbative result usingthe time derivative expansion procedure with again Eq.(17).

The major interest in our work comes from recent impetus in experiments conducted aboard spacecrafts[5-10]. For an *effective* gravitational acceleration of say $10^{-4}$ g, with g the value on the earth the predicted periods of oscillation according to Eq.(10) are in the order of the minute or two and according to Eq.(16) the temperature gradient at overstability of the order of one to ten °K/cm for mercury and other liquids, including water, open to air. Already these values agree well with experimental data extracted from transient solidification experiments done by Walter[10] with Selenium doped InSb aboard Skylab.

Aboard a spacecraft in a low/microgravity environment the crucial test of our predictions can be obtained by making an experiment with a water-alcohol solution around the minimum of surface tension *versus* temperature[11]. The suggested experiment is Bénard convection, *i.e.*, heating the layer from the liquid side before and past the surface tension minimum. Before the mimimum is reached one expects steady polygonal cells (Bénard cells) whereas past the minimum, *i.e.* in the region where the surface tension of the liquid solution increases with increasing temperature, oscillations are here predicted. As $\Delta$ (or $\delta$) contains the Marangoni number the suggested experiment defines a clear-cut test of our theory. Further details about this work will be given elsewhere[12].

## ACKNOWLEDGMENTS

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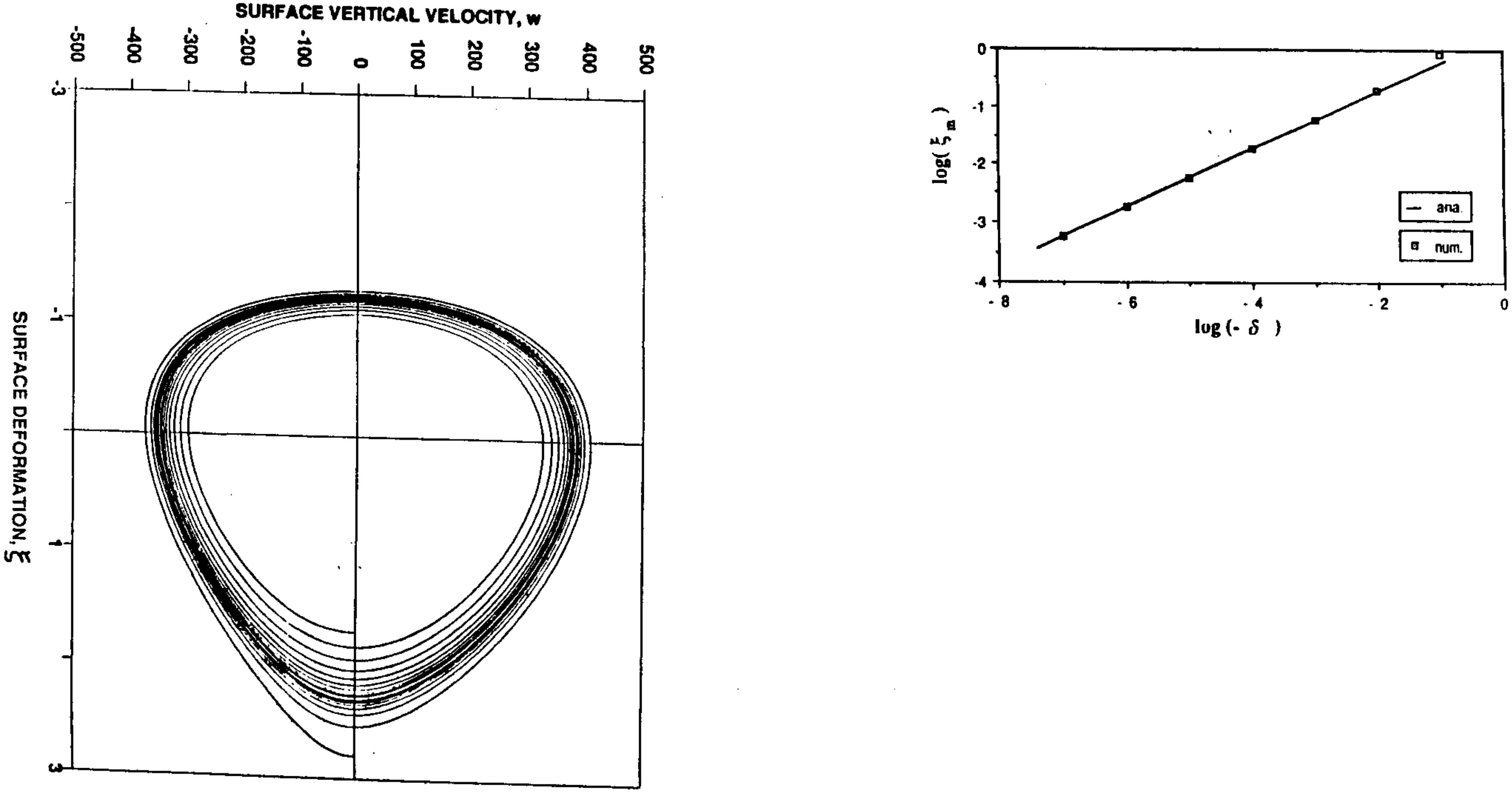
## CHU-VELARDE

## FIGURE CAPTIONS

**Fig. 1.** Limit cycle obtained from Eq.(15) for an initial condition either inside or outside the cycle. $\delta=-10$. A similar curve is obtained for all (not too large) values of $-\delta$ greater than zero.

**Fig. 2.** Log-log plot of the oscillation amplitude *versus* bifurcation parameter as we proceed into the supercritical region. Results correspond to the direct numerical integration (num.) and the singular perturbation analysis (ana.) of Eq.(17).

CHU & VELARDE: FIG. 2



SPACE-MODULATED OSCILLATION (TRANSVERSE PROBLEM) 7
APPROACH — LANDAU—GINSBURG PICTURE (MODEL)

BOUSSINESQ-LIKE EQ'NS

$$\frac{\partial \zeta}{\partial t} - w = \frac{-1}{a} w \frac{\partial^2 \zeta}{\partial x^2}$$

$$\frac{\partial w}{\partial t} = -a\left\{\frac{Bo}{PC} - \frac{1}{PC}\frac{\partial^2}{\partial x^2} + \frac{Ma}{P\sqrt{2\omega_0}}\frac{\partial^2}{\partial x^2}\right\}\zeta$$

$$-\left\{2a^2 - 2\frac{\partial^2}{\partial x^2} - \frac{Ma}{P\omega\sqrt{2P\omega_0}}\frac{\partial^2}{\partial x^2}\right\}\frac{\partial \zeta}{\partial t}$$

$$+ 8aw\frac{\partial^2}{\partial x^2}\zeta + 4a^3 w\zeta - a\left\{\frac{3}{2PC}\frac{\partial^2}{\partial x^2}\zeta\left(\frac{\partial}{\partial x}\zeta\right)^2\right\}$$

$$+ 5a^2 w\left(\frac{\partial}{\partial x}\zeta\right)^2$$

or in compact form (Landau- Ginsburg)

$$\frac{\partial \vec{x}}{\partial t} = M\vec{x} + DD^2\vec{x} + N(\vec{x})$$

$$\vec{x} = (\zeta, w)^T$$

$$M \equiv \begin{pmatrix} 0 & 1 \\ -\frac{Bo\, a}{PC} & -2a^2 \end{pmatrix}, \quad D \equiv \begin{pmatrix} 0 & 0 \\ \frac{a}{PC} - \frac{Ma^2}{P\sqrt{2P\omega_0}} & 2 + \frac{Ma}{P\omega_0\sqrt{2P\omega_0}} \end{pmatrix}$$

$$N \equiv \begin{pmatrix} -\frac{1}{a} w \frac{\partial^2 \zeta}{\partial x^2} \\ -\frac{3a}{PC}\frac{\partial^2}{\partial x^2}\zeta\left(\frac{\partial \zeta}{\partial x}\right)^2 + 8aw\frac{\partial^2}{\partial x^2}\zeta + 4a^3 w\zeta + 5a^2 w\left(\frac{\partial \zeta}{\partial x}\right)^2 + \left\{2a^2 - 2\frac{\partial^2}{\partial x^2} - \frac{Ma}{P\omega_0\sqrt{2P\omega_0}}\frac{\partial^2}{\partial x^2}\right\}\frac{w}{a}\frac{\partial^2 \zeta}{\partial x^2} \end{pmatrix}$$

INTERFACIAL OSCILLATORS / ... TIONS / — WAVES
TRANSVERSE (GRAVIT & CAPIL
LONGITUDINAL (THERMOCAPILLARY,...

STANDARD/TRADITIONAL HYDRODYNAMIC APPROACH

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  * AIR-LIQUID CASE*
  ** TRANSVERSE [(LAPLACE-KELVIN) & NON-LAPLACE] OSCILLATIONS/WAVES**
  *** LONGITUDINAL [ MARANGONI-LUCASSEN ] OSCILLATIONS/WAVES***
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  *LIQUID-LIQUID INTERFACE*
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  NONLINEAR SPACE MODULATED (LANDAU-GINSBURG / BOUSSINESQ-LIKE) OSCILLATION